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**STABILIZING MIXTURE TO PEROXIDE-BLEACHES FOR ZELLULOSEHALTIGER**

**MATERIALS** the invention relates to a stabilizing mixture to peroxide-bleach zellulosehaltiger materials, particularly from fabrics.

- 1 Peroxides, particularly Wasserstoffperoxyde, are often used bleaches for cellulosic fibers, which bottom addition of a stabiliser such as alkali silicates, particularly sodium silicate, used become.
- 2 During bleaching in presence of an alkali silicate and an hard water or contaminants on the crude commodity form heavy-soluble alkaline-earth silicates, which can settle on the good and cause thus stains and color reservations. The use of silicates as stabilisers leads other to the formation of a cementitious layer on the rollers and the bleaching equipments, which thereby regular replaced to become to have. Furthermore forms silica, which hot-bleaches during fixed become can. The grasp of the fabric bleached in presence of silicates becomes deteriorated therefore.
- 3 Bottom zellulosehaltigen materials come not only the fabrics into considerations, but also the zellulosehaltigen materials used to the papermaking such as groundwood and waste paper. In do not only peroxide-bleach these materials can the used alkali silicate by deposition the piping, flotation cells, sieves etc. clog, but also if the effectiveness of high-polymer aids such as Nassverfestiger and retention and drainage means, decrease and even the releasability aged offset printing colors worsen.
- 4 It was now found that one can avoid these disadvantages, if one as stabiliser of the peroxide a mixture, some Poly A hydroxyacrylsäure and/or - derivative and an other complexing water-soluble polymere carbonic acid contain, used.
- 5 Subject-matter of the instant invention is thus a stabilizing mixture, those A) a Poly A hydroxyacrylsäure, which monomers Units of formula I  
EMI.4.  
It contains where g 1 and R2 independently hydrogen or  
C1-Alkyl,  
R3 hydrogen or C1-5Alkyl, and  
M hydrogen or a cation mean and  
B) a water-soluble Homopolymerisat of the acryl or Methacrylsäure or copolymer of the acrylic acid with Methacryl acidic, acrylamide, methacrylamide, Acrylnitrili, Metr, acrylonitrile,  
Acrylic acid esters, methacrylic esters as well as anaeren äthylenisch unsaturated mono or dicarbonic acids of und Xoder Coopolymerisat from maleic acid and styrene, maleic acid and a vinyl ester or a maleic acid and a Vinyläther contain.
- 6 Those bottom A) mentioned Poly A hydroxyacrylsäuren are Homo or copolymers of the A-Hydroxyacrylsäuren, which contain the defined above units of formula I. The Poly A hydroxyacrylsäure can also in form of a Polylactonsvorliegen, which can become hydrolyzed and neutralized.
- 7 In the formula I g 1 and R2 mean hydrogen or methyl, whereby g 1 and R2 can be same or various, preferably preferably mean g 1 and R2 hydrogen. R3 preferably stands for hydrogen. M mean favourable-proves an alkali metal, for example to sodium or potassium, ammonium or substituted ammonium, for example the tri ethanol ammonium.
- 8 The average molecular weight of the polymers of A-Hydroxyacrylsäuren lies above approximate 300, favourable-proves between 5000 and 1000 000, preferably between 10,000 and 200,000.
- 9 When copolymers of the A-Hydroxyacrylsäuren one can use such, which contain only units of formula I, where at least one of these units of the other various is or such, which are polymerized with äthylenisch unsaturated comonomers.
- 10 Latter copolymers contain preferably at least 50% of the defined above units.
- 11 Preferred ones Poly A hydroxyacrylsäuren are those, which contain only units of formula I, the unsubstituted Poly A hydroxyacrylsäure in particular in salt form.
- 12 Those bottom B) of mentioned copolymers of the acrylic acid can up to 50 Gew.-%, preferably from 1 to 20 Gew.-% äthylenisch unsaturated compounds copolymerizable with acrylic acid contain.
- 13 The copolymers can contain also several in-polymerized comonomers. As äthylenisch unsaturated mono or dicarbonic acid e.g. come. Crotonic acid and itaconic acid in considerations.
- 14 Those bottom B) of maleic acid copolymers mentioned are present major in the molar ratio 1:1. As vinyl esters one can use for example vinyl acetate and vinyl propionate. Suitable Vinyläther e.g. is: C1-4Alkylvinyläther.
- 15 The molecular weight of the polymers or copolymers B) lies generally between 500 and 5,000,000, particularly 1000 and 1,000,000, whereby top ranges between 5000 and 500,000 prefered are.
- 16 The polymers and copolymers B) become favourable-prove applied in form of an alkali, an ammonium or an amine salt. These salts can either by polymerizing corresponding monomers and/or, salts comonomer or by at least partial neutralizing of the polymers and/or. Copolymers with alkali hydroxides and/or. Ammonia or amines obtained becomes. As amines come methylamine, ethyl amine, dimethylamine, tri ethyl amine, the ethanol amine etc. in considerations.

- 17 The mixture according to invention preferably contains the components A) and of B) in a weight ratio A: B by 1:0.2 - 5.
- 18 Additional one to A) and B) knows the mixture according to invention still other components, for example other complexing agents C) and a hydrotropes product D) contain.
- Bottom complexing agent C) is to be understood both a single complexing agent and a mixture from two or several complexing agents to. Suitable complexing agents are favourable-prove organic sequestering agents like e.g. Aminocarbonic acids and their salts as for example Acetylendiamintetraessigsäure or Diäthylentriaminpentaeissigsäure, hydroxycarboxylic acid and their salts as for example Glukonsäure, Glukoheptensäure or lactic acid. Organophosphon of acidic approximately their salts as for example Diäthylentriaminpenta (phosphonic acid/phosphonic acid phosphonic acid), I-Hydroxyäthylen-I, I-diphosphonsäure or Aethylendiamintetra (phosphonic acid/phosphonic acid phosphonic acid) or monomers polycarboxylic acids such as citric acid, tartaric acid or malonic acid and their salts.
- 20 Prefered ones are particularly the Acetylendiamintetraessigsäure and their salts.
- 21 The hydrotropes product D) is appropriately a product, which possesses also the properties of an electrolyte and/or a solubilizer. As suitable products for example urea, alkanolamines such as tri ethanol amino or a low alcohol comes such as isopropanol into question.
- A preferred stabilizing mixture according to the invention is the for example subsequent, those
- 22 100 parts of the component A  
20 to 500 parts of the component B  
10 to 300 parts of the component C  
30 to 200 parts of the component D contains.
- 23 The mixture according to invention becomes ago provided after known methods, preferably by simple mixing of the components. Those Component C) can either in at least more partially neutralized  
Salt form used or in the mixture at least partially neutralized will become, for example by addition of a basic Compound. Preferably the components of the mixture in the same salt form become used.
- 24 The stabilizing mixture becomes appropriately as aqueous  
Mixture, preferably in form of a preparation, from 20 to 90% water contained can do, used.
- 25 Subject-matter of the instant application is an other method to peroxide-bleaches of zellulosehaltigen materials, characterised in that one the materials with a Bleichflotte treated, which contains a stabilizing mixture like described above, and in this way bleached zellulosehaltigen materials.
- 26 The peroxide bleaching process becomes conducted in the alkaline range after known methods. As peroxide hydrogen peroxide becomes preferably used.
- Within the textile range the zellulosehaltige fabric becomes appropriately with a fleet, which contains the hydrogen peroxide in the conventional amounts and the mixture according to invention, in a Kontinieverfahren, for example PAD roll, PAD Steam or PAD batch or a batch process, for example in a skid, in the Jigger or jet treated. After that bleaches the fabric becomes after known methods other-treated.
- 28 If groundwood or waste paper becomes bleached, the treatment becomes preferably conducted between 30 and 60 ° C. Bleaches either in the pulper or in a Bleichturm on continuous or discontinuous manner conducted can become.
- 29 The stabilizing mixture according to the invention becomes in amounts from 0,05 to 6%, preferably from 0,05 to 4% (calculated on that Fabric), used.
- 30 For groundwood-peroxide-bleach preferably becomes the stabilizing mixture in an amount from 0,15 to 1,5% (calculated on atro - groundwood) used. For the De-Inken from waste paper the stabilizing mixture becomes, preferably in an amount of 0,1 to 1% (calculated on atro waste paper), the Bleichbad added.
- 31 In the case peroxide-bleach the groundwood and/or. Waste paper, the stabilizing mixture can replace that completely or partly conventional wise used alkali silicate. As example of such  
Mixture knows one a Bleichflotte, the 0,1 to 0,6% of the mentioned above mixture as well as 0,5 to 2,0% sodium water glass 380 Be contains, use.
- 32 The bottom term "waste paper" the conventional waste paper mixtures become such as daily papers, mixtures from daily papers and illustrated ones, printed computer paper and offset newspapers referred. That old one paper becomes first conditioned and then bleached according to invention and/or. deinked.
- 33 The groundwood can after known methods, as usual in that  
Paper industry from various origin prepared become.
- 34 After that bleaches after the resultant Stoffsuspension becomes knew methods processed.
- 35 The stabilizing mixture becomes preferably for silicate a free hydrogen peroxide-bleaches zellulosehaltiger fabrics used.
- Additional one to the stabilizing preparation knows the Bleichflotte still other aids, as anionic or not ionogene surfactants contain. It is favourable that the Bleichflotte Mg+ + contains and if necessary approx. ions. Thus it is possible to use hard water or a magnesium and if necessary a calcium salt, for example magnesium chloride or sulfate to admit to the fleet.
- 37 The zellulosehaltigen fabrics can consist of natural or regenerated cellulose, and/or. are present in mixtures with syntheti schen fibers such as polyesters.
- The so bleached zellulosehaltigen materials point a good
- 38 Whiteness up. The bleached fabrics possess an other soft touch and a good Hydrophilie. The out old paper recovered paper is from good quality and can for various purposes again used become. Additional one to its stabilizing effect has the preparation according to invention still another anti-catalytic effect against catalysts how Fe3+ and Cu2+ ions. Furthermore this preparation protects the cellulose from a degradation of the degree of polymerization.
- 39 The subsequent examples describe the method. Parts are  
Parts by weight or volume parts, percents are weight percentage and temperatures are in centigrades indicated.
- 40 Example 1  
45 parts one of Poly A hydroxyacrylsäure descending

- 42 Polylactons (mg, ~ 50.000)  
100 parts EDTA in sodium salt form  
50 parts of a polyacrylic acid as sodium salt (MGN 500.000) and  
40 parts urea become in hard water (5 dH Mg<sup>2+</sup>) dissolved and with hard water on 100 parts diluted (referred as mixture A).
- 43 After addition of 30 parts of a commercial anionic surfactant and 300 parts H2O2 35% the mixture becomes on 1000 parts diluted and on pH approx. 13 with sodium hydroxide adjusted.
- 44 Entschichtete 100% cotton Krettonne is geklotzt with this fleet and squeezed off on 100%. Afterwards the fabric becomes rolled and during 90 minutes with 950 treated. After warm and cold bobbins one receives a white Krettonne with a soft touch.
- Example 2  
45 45 parts one of Poly A hydroxyacrylsäure descending  
Polylactons (mg ~ 50.000)  
100 parts EDTA in sodium salt form  
40 parts of a polyacrylic acid as sodium salt (mg > , 100.000) and  
25 parts urea become in hard water (5 dH Mg<sup>2+</sup>) dissolved and with hard water on 100 parts diluted (referred as mixture B).
- 46 After addition of 30 parts of a commercial anionic surfactant and 350 parts H2O2 35% the mixture becomes on 1000 parts diluted and on pH ca.13 with sodium hydroxide adjusted.
- 47 Entschichtete 100% cotton Krettonne is geklotzt with this fleet and squeezed off on 100%. Afterwards the fabric becomes during 20 minutes at 1020 damped. After warm and cold bobbins one receives a Krettonne with high whiteness.
- Example 3 in a pulper is registered a bleaching solution, those by 1000 parts  
48 100 parts mixture A or B  
25,0 parts Natriumperoxid of 60 volume. %  
0,3 parts of a commercial alkoxylated, more quater nieren alkyl diamine and  
40,0 parts NaOH 30% contains.
- 49 A waste paper mixture existing from 100% daily papers in this bleaching solution one registers and with 45-55 and a pH value from 10-11 to a Stoffdichte from 4 to 6% impacted.
- 50 Short one before Pulperschluss becomes 1 part of a commercial collecting tank, for example 1 part oleic acid, the Bleichbad added and the subsequent Stoffsuspension into a drain wash tub passed and during 1 to 2 hours weak agitated. Afterwards the Stoffsuspension cleaned, and diluted, is entstippt the flotation cells supplied and then processed.
- 51 A bleached paper of good quality becomes so obtained.



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### STABILIZING MIXTURE TO PEROXIDE-BLEACHES ZELLULOSEHALTIGER MATERIALS

#### Claims

1. A stabilizing mixture, contained  
A) a Poly A hydroxyacrylsäure, which monomers  
Units of formula I  
EMI 1.1  
it contains where g 1 and R2 independently hydrogen or C1~5Al kyl,  
R3 hydrogen or c1 5Alkyl, and  
M hydrogen or a cation mean and  
B) a water-soluble Homopolymerisat of the acryl or Methacrylsäure or copolymer of the acrylic acid with Methacryl acidic, acrylamide, Methacrylimid, acrylonitrile, methacrylonitrile,  
Acrylic acid ester, methacrylic ester as well as other äthylenisch unsaturated mono or dicarboxic acids and/or copolymer from maleic acid and styrene, maleic acid and one vinyl ester or maleic acid and a Vinyl ethers.
2. A mixture in accordance with claim 1, characterised in that the components A and B in a weight ratio A: B of 1:0.2 - 5 contains.
3. A mixture in accordance with claims 1 and 2, thus gekenn draws that it contains additional still other complexing agents and a hydrotropes product.
4. Method to peroxide-bleaches the materials with one from zellulosehaltigen materials, characterised in that one Bleichflotte treated, which contains a stabilizing mixture of according to claim 1.
5. Method in accordance with claim 4, characterised in that one zellulosehaltige fabrics with a silicate-free Hydrogen peroxide bleaching fleet treated, which contains a stabilisie rende mixture of according to claim 1.
6. Zellulosehaltige materials, bleached 1 according to claim in presence of a stabilizing mixture.